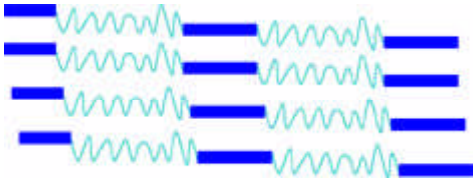
Novel Molecular Architectures Developed for Improved Solid Polymer Electrolytes for Lithium Polymer Batteries

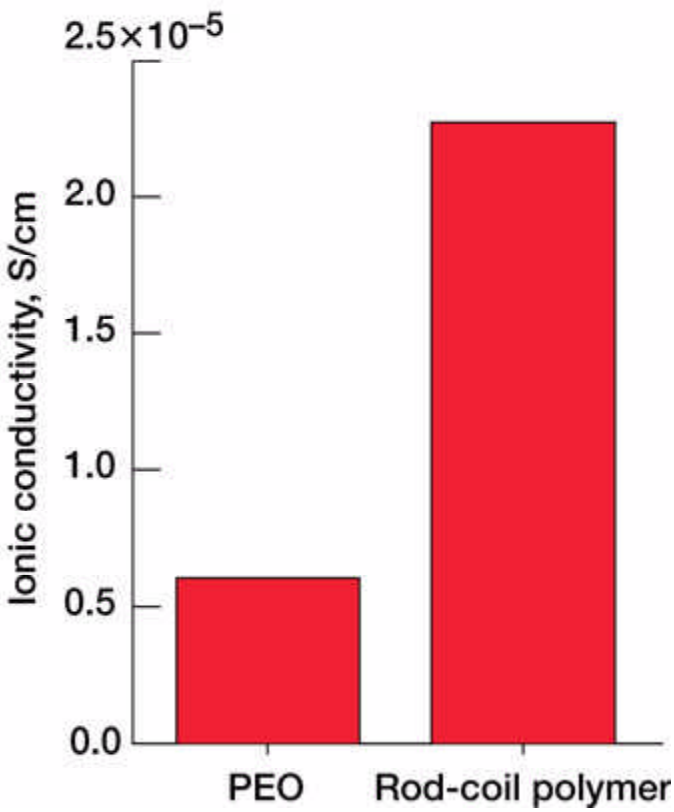


Structure of rod-coil polymers showing phase separation between incompatible rigid rods and flexible ion-conducting coils.

Lithium-based polymer batteries for aerospace applications need the ability to operate in temperatures ranging from -70 to 70 °C. Current state-of-the-art solid polymer electrolytes (based on amorphous polyethylene oxide, PEO) have acceptable ionic conductivities (10^{-4} to 10^{-3} S/cm) only above 60 °C. Higher conductivity can be achieved in the current systems by adding solvent or plasticizers to the solid polymer to improve ion transport. However, this can compromise the dimensional and thermal stability of the electrolyte, as well as compatibility with electrode materials. One of NASA Glenn Research Center's objectives in the PERS program is to develop new electrolytes having unique molecular architectures and/or novel ion transport mechanisms, leading to good ionic conductivity at room temperature and below without solvents or plasticizers.

It is widely held that ionic conductivity is highest for amorphous (noncrystalline) polymers with low glass-transition temperatures. This is thought to be because strong coulombic forces and low free volume trap the ions in the crystalline regions. However, promising new approaches to less temperature dependent ionic conductivity in solid polymers include ways of introducing free volume and short-range order, if not crystallinity, into the system. Some of these approaches include Langmuir-Blodgett films, liquid crystals, and self-assembling monolayers.

We are combining several of these approaches to investigate new polymers with novel architectures for stable, processable polymer electrolytes with enhanced ionic conductivity over a wide range of temperatures. One approach under investigation in-house is a series of rod-coil block copolymers in which rigid polyimide rods alternate with very flexible, short PEO strands. Because of the incompatibility between the rods and coils, the blocks would tend to phase separate as much as possible. This leads to the formation of nanoscale channels of ionically conducting PEO alternating with the rigid polyimide rods. The rod regions form the mechanical support for conducting PEO coils, resulting in films with both good conductivity and mechanical integrity.



Comparison of room-temperature ionic conductivity of state-of-the-art PEO with that of a polyimide rod-coil polymer.

Rod-coil polyimides doped with lithium salts form rubbery films having glass-transition temperatures around -50 °C. Polymers with room-temperature conductivities as high as 2.3310^{-5} S/cm have been synthesized. This is almost an order of magnitude better than measured state-of-the-art PEO. Rod-coil polymers are easily cast from 40-wt% solutions and cured into flexible, solvent-free films by heating to 200 °C. The films could be cast directly onto electrode substrates or handled as free-standing films, offering flexibility in battery fabrication.

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